

NVU perspective on simple liquids' quasiuniversality

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The last half century of research into the structure, dynamics, and thermodynamics of simple liquids has revealed a number of approximate universalities. This paper argues that simple liquids' reduced-coordinate constant-potential-energy hypersurfaces constitute a quasiuniversal family of compact Riemannian manifolds, which is parameterized by a single number. From this follows the previously discussed quasiuniversalities.

I. INTRODUCTION

By their contrast to complex liquids [1–6], simple liquids are traditionally defined as systems of spherically symmetric particles interacting via pair forces [6–16]. A number of such systems, however, like the Gaussian core model [17–20], the Lennard-Jones Gaussian model [21], the Jagla and related discontinuous-force models [22–25], and others [25–29] exhibit quite complex behavior. On the other hand, van der Waals *molecular* liquids are generally regular and “simple” in their properties [6, 15]. In view of these facts we recently suggested [30] defining instead liquid simplicity from the property of strong correlations between equilibrium virial and potential energy fluctuations in the NVT ensemble [31–35]. This is how the term “simple liquid” is used below. In practice there is considerable overlap between the two definitions, for instance the Lennard-Jones liquid and related systems are simple in both senses. One notable difference, however, is that realistic liquids are only simple in the present meaning of the term in part of their phase diagram – simplicity does not apply near or at the critical point or at supercritical and gas states (where different kinds of simplicity apply, of course). With regard to real liquids, it appears that most or all van der Waals bonded and metallic liquids are simple, whereas covalently bonded, hydrogen-bonded, and strongly ionic liquids are generally not simple because competing interactions weaken the virial potential-energy correlations [30].

Simple liquids are characterized by having isomorphs in their phase diagram [34]. An isomorph is an equivalence class of the following equivalence relation: two state points are isomorphic if all pairs of physically relevant microconfigurations of the state points, which trivially scale into one another, have the same configuration-space canonical probability. Only inverse-power-law (IPL) potentials have exact isomorphs, but all strongly correlating liquids have isomorphs to a good approximation [34].

Simple liquids' simple properties derive from the fact that the existence of isomorphs implies that the phase diagram is effectively one-dimensional instead of two-dimensional for the several properties that are isomorph

invariant. Examples of such properties are [34]: Newtonian and Brownian reduced-unit dynamics, reduced-unit static structure factors of any order, the excess entropy, the isochoric heat capacity. Another example is that for any simple liquid melting defines an isomorph in the phase diagram. This implies invariance along the melting curve of, e.g., excess entropy, reduced viscosity, reduced heat conductivity, reduced diffusion constant, etc, as well as invariance of the Lindemann melting criterion [34, 35].

The isomorph theory explains a number of previously noted regularities relating to any given simple liquid [34]. The theory, however, cannot explain the several intriguing similarities between *different* simple liquids known for a long time. This is the focus of the present paper, which views simple-liquid quasiuniversality from an NVU perspective.

NVU dynamics [36], which is inspired by earlier approaches to dynamics conserving [37, 38] or limiting [39] the potential energy, is defined as geodesic motion on the constant-potential-energy hypersurface. If $\mathbf{R} \equiv (\mathbf{r}_1, \dots, \mathbf{r}_N)$ is the $3N$ -dimensional position vector describing a system of N particles, \mathbf{R}_i the position vector at time step i , and \mathbf{F}_i the corresponding $3N$ -dimensional force vector, the NVU algorithm [36] is $\mathbf{R}_{i+1} = 2\mathbf{R}_i - \mathbf{R}_{i-1} - 2[\mathbf{F}_i \cdot (\mathbf{R}_i - \mathbf{R}_{i-1})]\mathbf{F}_i/\mathbf{F}_i^2$. As shown in Ref. 40, if m is the particle mass and Δt the time step of the Verlet algorithm $\mathbf{R}_{i+1} = 2\mathbf{R}_i - \mathbf{R}_{i-1} + \mathbf{F}_i(\Delta t)^2/m$, the NVU and Verlet algorithms are equivalent in the thermodynamic limit because the fluctuations of the NVU -force prefactor become insignificant as $N \rightarrow \infty$. Consequently, the radial distribution function, diffusion constant, coherent and incoherent intermediate scattering functions, etc, are identical in the thermodynamic limits of NVU and standard NVE or NVT Newtonian dynamics. This has been confirmed in computer simulations of atomic as well as molecular models [36, 40, 41].

NVU dynamics provides an alternative view of a liquid's molecular dynamics. At any given state point all information about the liquid's structure and dynamics is encoded in its constant-potential-energy hypersurface Ω . If $\langle U \rangle$ is the average potential energy at the state point, this compact Riemannian differentiable manifold is defined by

$$\Omega \equiv \{\mathbf{R} \mid U(\mathbf{R}) = \langle U \rangle\}. \quad (1)$$

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Ω is a so-called level set of the function $U(\mathbf{R})$. If standard periodic boundary conditions are employed, Ω is embedded as a $(3N - 1)$ -dimensional hypersurface in the $3N$ -dimensional torus. The manifold Ω is not only defined for simple liquids, of course, but for all liquids – in fact also for all solids and gasses.

The present paper considers systems of N identical particles in volume V interacting via pairwise additive forces. Thermodynamic quantities are excess quantities, i.e., in excess of the corresponding ideal gas quantities at the same density and temperature. Thus S is the *excess* extensive entropy ($S < 0$) and C_V the *excess* extensive isochoric specific heat, which we refer to as just “entropy” and “specific heat”. The corresponding intensive quantities are denoted by lower-case letters, i.e., $s \equiv S/N$ and $c_V \equiv C_V/N$. Reduced quantities are marked by a tilde.

It is clear from the results of many years of research into the liquid state that there is no such thing as absolute universality, even among narrowly restricted classes of liquids. Thus any theory predicting liquid-state universality invariably breaks down because it is too simple. The philosophy of this paper is that quasiuniversalities provide useful insights, even though these are known from the outset to be only approximate. In this connection it is an obvious conjecture that genuine simple-liquid universality is approached as the spatial dimension increases towards infinity – if this is the case, we have for liquids a situation reminiscent of that of critical phenomena.

Section II argues for the existence of a quasiuniversal family of constant-potential-energy hypersurfaces for simple liquids, parameterized by just one parameter. The argument presented is not rigorous, but meant to suggest one possible route for justifying quasiuniversality. The reader may choose to accept quasiuniversality in its NVU formulation as a postulate, skip Sec. II, and proceed to Sec. III that derives and discusses a number of consequences of the NVU formulation of simple liquids’ quasiuniversality. Section IV returns to the question of what causes quasiuniversality. Finally, Sec. V gives a brief summary.

II. A SINGLE-PARAMETER FAMILY OF HYPERSURFACES COMMON TO ALL SIMPLE LIQUIDS

Any state point in the phase diagram of a liquid gives rise to a constant-potential-energy hypersurface Ω as defined in Eq. (1). At first sight these manifolds may appear to be completely characterized by the single number $\langle U \rangle$, but actually the system volume V is a second parameter that is implicit in the definition of $U(\mathbf{R})$. Thus for liquids in general, Ω is described by two parameters, corresponding to the two dimensions of phase space. Another way of seeing this is to write the pair potential as $v(r) = \varepsilon \phi(r/\sigma)$; it is then clear that any given state point gives rise to two dimensionless numbers characterizing the state point’s reduced-coordinate constant-potential-

energy hypersurface $\tilde{\Omega}$, namely $\sigma^3 \rho$ (where $\rho = N/V$ is the particle density) and $\varepsilon/k_B T$.

Using reduced units means measuring length in units of $\rho^{-1/3}$, time in units of $\rho^{-1/3} \sqrt{m/k_B T}$, and energy in units of $k_B T$. The reduced $3N$ -dimensional position vector is thus defined by $\tilde{\mathbf{R}} \equiv \rho^{1/3} \mathbf{R}$. Appendix A of Ref. 34 showed that a liquid has strong virial potential-energy correlations (i.e., is simple) if and only if the liquid has good isomorphs, and that this happens if and only if the liquid’s reduced-unit constant-potential-energy hypersurfaces are invariant along certain curves in the phase diagram (the isomorphs). Thus for any given simple liquid a single number, λ , parameterizes the reduced-coordinate constant-potential-energy hypersurfaces. We indicate this by writing

$$\tilde{\Omega} = \tilde{\Omega}(\lambda) \quad (2)$$

where

$$\tilde{\Omega} \equiv \{ \tilde{\mathbf{R}} \mid U(\rho^{-1/3} \tilde{\mathbf{R}}) = \langle U \rangle \}. \quad (3)$$

The isomorph theory says nothing about how these hypersurfaces compare between different simple liquids. We now argue that the family $\tilde{\Omega}(\lambda)$ is quasiuniversal, i.e., approximately the same for all simple liquids.

The only systems with 100% correlation between NVT equilibrium fluctuations of virial ($W \equiv -1/3 \sum_i \mathbf{r}_i \cdot \nabla_i U$) and potential energy are the inverse-power-law (IPL) systems, for which the potential energy scales with interparticle distance as $\propto r^{-n}$. For these systems the 100% correlation follows from the identity $U(\lambda \mathbf{R}) = \lambda^{-n} U(\mathbf{R})$ and Euler’s theorem for homogeneous functions. A simple liquid by definition has strong WU correlations. This implies that at each of its strongly correlating state points the liquid behaves much like an IPL system. The value of the effective IPL exponent n generally varies with state point. For Lennard-Jones (LJ) liquids at typical state points n is fairly constant, between 5 and 6. For the 99.9% correlating “repulsive LJ liquid” defined by the pair potential $\epsilon[(r/\sigma)^{-12} + (r/\sigma)^{-6}]$ [42], the exponent varies from $n \cong 12$ at high densities to $n \cong 6$ at low densities. How much the effective IPL exponent varies throughout the phase diagram, however, is of no importance for the below arguments for $\tilde{\Omega}(\lambda)$ quasiuniversality.

IPL systems with different exponents have very similar (“quasiuniversal”) behavior. This was noted a long time ago in relation to these systems’ structure and DC dynamic properties expressed, e.g., via the diffusion constant [43–51]. During the last decade IPL quasiuniversality has come into focus again [52–54] and been extended to include general dynamic properties, termed “dynamic equivalence” by Medina-Noyola and coworkers. Dynamic equivalence has been established for Brownian [55, 56] as well as Newtonian [57–60] dynamics.

Because structure and dynamics are both encoded in $\tilde{\Omega}$, IPL quasiuniversality follows if all IPL systems have

almost identical constant-potential-energy hypersurfaces. But why should this be the case? To understand this, we consider two infinitesimally close configurations with same n -IPL potential energy and show that they for all m to a good approximation have the same m -IPL potential energy.

The m -IPL potential energy is given by $U_m = \varepsilon_m \sum_{ij} (r_{ij}/\sigma)^{-m}$, in which r_{ij} is the distance between particles i and j . The change in U_m between two nearby configurations is given by

$$\delta U_m = -m \varepsilon_m \sum_{ij} \left(\frac{r_{ij}}{\sigma} \right)^{-m-1} \frac{\delta r_{ij}}{\sigma}. \quad (4)$$

From this it follows that

$$\frac{d}{dm} \left(\frac{\delta U_m}{m \varepsilon_m} \right) = \sum_{ij} \left(\frac{r_{ij}}{\sigma} \right)^{-m-1} \ln \left(\frac{r_{ij}}{\sigma} \right) \frac{\delta r_{ij}}{\sigma}. \quad (5)$$

The factor $\ln(r_{ij}/\sigma)$ in Eq. (5), which does not vary much because it is a logarithm, is multiplied by the factor $(r_{ij}/\sigma)^{-m-1}$ that varies a lot. The product will be dominated by a rather narrow range of interparticle distances, the most important of which is denoted by $\langle r \rangle_m$, a quantity that depends on state point and m . As a good approximation one can replace $\ln(r_{ij}/\sigma)$ by $\ln(\langle r \rangle_m/\sigma)$, and Eq. (5) now becomes

$$\frac{d}{dm} \left(\frac{\delta U_m}{m \varepsilon_m} \right) = -\ln \left(\frac{\langle r \rangle_m}{\sigma} \right) \left(\frac{\delta U_m}{m \varepsilon_m} \right). \quad (6)$$

Recall that $\delta U_n = 0$. Since $\delta U_m/(m \varepsilon_m) = 0$ is the unique solution to this first-order differential equation that obeys $\delta U_n = 0$, it follows that $\delta U_m = 0$ for all m . – Note that the approximation made in replacing $\ln(r_{ij}/\sigma)$ by a constant is questionable when $m \leq 2$, in which case no narrow range of interparticle distances dominates Eq. (5) because $\sum_j r_{ij}^{-m-1}$ diverges.

Within the above approximation the potential-energy functions $U_n(\mathbf{R})$ have the same constant-potential-energy hypersurfaces for all $n \geq 2$. Possibly, this applies for all n . Since a simple liquid at a given state point may be approximated by an IPL system, this means that all simple liquids have approximately the same constant-potential-energy hypersurfaces. In other words, to a good approximation a single family of manifolds parameterized by one parameter, $\tilde{\Omega}(\lambda)$, is common to all simple liquids. Each isomorph of a simple liquid corresponds to a particular value of λ , i.e., to one specific manifold $\tilde{\Omega}$.

III. CONSEQUENCES OF $\tilde{\Omega}(\lambda)$ QUASIUNIVERSALITY

Different IPL systems exhibit close similarities with respect to structure and dynamics, similarities that extend

to all other simple liquids [43–70]. Because reduced-unit structure and dynamics are both encoded in $\tilde{\Omega}$, any two state points of two different IPL systems with same $\tilde{\Omega}$ have the same structure and dynamics. The extension of similarities to all simple liquids follows from $\tilde{\Omega}(\lambda)$ quasiuniversality. Note that the hard-sphere (HS) system also exhibits these quasiuniversalities because it is the $n \rightarrow \infty$ limit of the n -IPL system.

The Young-Andersen approximate scaling principle [57, 58]. This principle states that if two liquids at two state points have the same reduced-unit radial distribution function $g(\tilde{r})$, they have the same reduced-unit dynamics. $g(\tilde{r})$ is determined from $\tilde{\Omega}$, so having the same $g(\tilde{r})$ implies having the same $\tilde{\Omega}$. This implies same dynamics.

Quasiuniversality of the order-parameter maps of Debenedetti and coworkers [71–73]. Plotting a translational order parameter versus an orientational order parameter for various state points leads to a one-dimensional curve for any simple liquid, because both order parameters are isomorph invariant [34]. The approximate identity between order-parameter curves of different simple liquids follows from $\tilde{\Omega}(\lambda)$ quasiuniversality, since $\tilde{\Omega}$ determines both order parameters.

Excess entropy scaling [74–77]. Rosenfeld noted in 1977 that the reduced-unit diffusion constants \tilde{D} of different simple liquids have an approximately universal dependence on the entropy per particle, s [74]. This type of quasiuniversality applies also, e.g., for the heat conductivity as a function of excess entropy [78]. For any simple liquid, since both \tilde{D} and s are isomorph invariant, one quantity is a function of the other. Quasiuniversality of the function $\tilde{D}(s)$ is a consequence of the fact that \tilde{D} and s are both encoded in $\tilde{\Omega}$ (the entropy $S = Ns$ is the logarithm of the area of $\tilde{\Omega}$).

The Lindemann melting criterion [79–81]. According to the Lindemann criterion a crystal melts when the vibrational mean-square displacement obeys $\sqrt{\langle \tilde{x}^2 \rangle} \simeq 0.1$ where $\tilde{x} = x\rho^{1/3}$ in which x is the atomic vibrational displacement from equilibrium in an axis direction. The melting curve in the phase diagram is an isomorph [34, 35], so melting takes place for a particular manifold $\tilde{\Omega}_c$ of the crystalline state. This manifold determines $\langle \tilde{x}^2 \rangle$. Thus any simple crystal melts when $\langle \tilde{x}^2 \rangle$ reaches a certain, quasiuniversal value. The Lindemann criterion and generalizations [79, 81, 82] have been criticized on the grounds that they are single-phase criteria, whereas melting occurs when the crystal and liquid free energies are the same, so any melting criterion should involve both phases. One possible resolution of this paradox is that the Lindemann criterion does not, in fact, determine the melting line, but a spinodal at a slightly higher temperature where the crystal becomes mechanically unstable [83, 84]. Alternatively, for the class of simple liquids, $\tilde{\Omega}$ quasiuniversality implies that there is basically just one melting process, which takes place at the state point where the specific crystalline manifold is $\tilde{\Omega}_c$. Any single-

phase melting criterion referring to this manifold applies universally for simple liquids.

Melting rules referring to the liquid. Quasiuniversality of these follow from the fact that $\tilde{\Omega}$ is quasiuniversal also on the liquid side of melting. For instance, this implies the Hansen-Verlet rule that a liquid crystallizes when the first peak of the radial distribution function reaches the value 2.85 [44]. Likewise, any simple liquid's c_V is close to $3k_B$ at freezing [85, 86] (it is shown below that c_V is encoded in $\tilde{\Omega}$). Other quasiuniversal melting rules similarly follow from $\tilde{\Omega}(\lambda)$ quasiuniversality [82]. Examples are the Andrade equation from 1934 predicting a quasiuniversal value of the reduced-unit melting point viscosity [87, 88], the Raveche-Mountain-Street criterion [89] of a quasiuniversal value of the ratio between the values of the maximum and minimum of the radial distribution function at freezing, Lyapunov-exponent based criteria [83], or the criterion of zero higher-than-second-order liquid configurational entropy at crystallization [90]. Note that the theory predicts a quasiuniversal constant-volume melting entropy for simple liquids, which is consistent with experiment [85, 91]. – We finally mention the Egelstaff-Widom quasiuniversality [92], according to which the isothermal compressibility times the liquid surface tension is almost constant for liquids close to the triple point, equal to a few tenths of Angstroms. By the compressibility theorem the reduced isothermal compressibility is an isomorph invariant. Thus the Egelstaff-Widom quasiuniversality follows if the reduced surface tension is also an isomorph invariant, which is likely the case.

Algebraic closedness properties of the class of simple potentials. Suppose $U_1(\mathbf{R})$ and $U_2(\mathbf{R})$ are both potentials of simple liquids, i.e., strongly correlating. Then their sum $U_1(\mathbf{R}) + U_2(\mathbf{R})$ and product $U_1(\mathbf{R})U_2(\mathbf{R})$ are also strongly correlating potentials. This does not follow merely from the property of strong correlation between virial and potential energy NVT equilibrium fluctuations, but from the quasiuniversality of simple liquids: Since $U_1(\mathbf{R})$ and $U_2(\mathbf{R})$ are both constant on the manifolds $\tilde{\Omega}(\lambda)$, this applies also for their sum and product. In particular, note the following property. Writing a simple pair potentials as $v(r) = \varepsilon\phi(r/\sigma)$, the derivative with respect to σ , $\partial v(r)/\partial\sigma$, is also simple.

Additivity of thermodynamic quantities. Suppose $U(\mathbf{R}) = U_1(\mathbf{R}) + U_2(\mathbf{R})$ in which $U_1(\mathbf{R})$ and $U_2(\mathbf{R})$ define a simple liquid; an example is when $U(\mathbf{R})$ is the LJ potential, $U_1(\mathbf{R})$ is an $n = 12$ IPL function, and $U_2(\mathbf{R})$ is minus an $n = 6$ IPL. Then $U(\mathbf{R})$ defines a simple liquid, and as functions of density and entropy the corresponding temperatures obey $T(\rho, S) = T_1(\rho, S) + T_2(\rho, S)$ [93]. To show this, note that since the entropy determines $\tilde{\Omega}$, at given values of ρ and S the three constant-potential-energy manifolds are identical: $\Omega = \Omega_1 = \Omega_2$. This implies that $U(\rho, S) = U_1(\rho, S) + U_2(\rho, S)$, from which the required $T(\rho, S) = T_1(\rho, S) + T_2(\rho, S)$ follows from the definition of temperature $T = (\partial U/\partial S)_\rho$. The thermodynamic relation $W = (\partial U/\partial \rho)_S$ similarly implies additivity of virials: $W(\rho, S) = W_1(\rho, S) + W_2(\rho, S)$.

The (excess) Helmholtz free energy F , (excess) Gibbs free energy G , and (excess) enthalpy H are likewise also additive: $F(\rho, S) = F_1(\rho, S) + F_2(\rho, S)$, $G(\rho, S) = G_1(\rho, S) + G_2(\rho, S)$, $H(\rho, S) = H_1(\rho, S) + H_2(\rho, S)$.

An application is “additivity of melting temperatures” [49]: Since crystallization for all simple liquids takes place at a certain value of the liquid entropy, at any given density one has $T_m = T_{m,1} + T_{m,2}$. An IPL liquid's melting temperature scales with density as $T_m \propto \rho^{n/3}$, so for the LJ liquid an expression of the form $T_m = A\rho^4 - B\rho^2$ applies [42, 49, 94].

A quasiuniversal equation of state. It was recently shown that simple liquids have simple thermodynamics in the sense that temperature factorizes into a product of a function of entropy and a function of density, $T = f(s)h(\rho)$ [42]. We now show that the function $f(s)$ is quasiuniversal. This justifies writing the equation of state as

$$T = f_0(s)h(\rho). \quad (7)$$

The point is that the specific heat, like the entropy, depends only on the geometry of $\tilde{\Omega}$ and not, for example, on the specific details of the potential or the temperature. This can be shown by first writing c_V in terms of fluctuations of canonical ensemble probabilities, and then relating the latter to microcanonical (NVU) probabilities. According to Einstein $C_V = \langle(\Delta U)^2\rangle/k_B T^2$ in which the average refers to the canonical ensemble. In terms of the configuration-space probability $p \propto \exp(-U/k_B T)$ this may be written $C_V = k_B \langle(\Delta \ln p)^2\rangle$. The canonical ensemble is realized from the microcanonical NVU ensemble in the usual textbook way by considering a small subvolume V_m of the total volume V . On average V_m contains m particles where $m/N = V_m/V$. Each configuration of m particles in V_m , $(\mathbf{r}_1, \dots, \mathbf{r}_m)$, has a probability $p(\mathbf{r}_1, \dots, \mathbf{r}_m)$ that can be calculated from the manifold Ω (or $\tilde{\Omega}$) by integrating out the remaining degrees of freedom. In the microcanonical ensemble this corresponds to the volume of the lower-dimensional cut of Ω corresponding to fixing the positions of particles 1 to m , and $p(\mathbf{r}_1, \dots, \mathbf{r}_m)$ is therefore a purely geometric quantity. More accurately, we argue as follows. The set of configurations in Ω with *precisely* m particles in volume V_m is denoted by $\Omega_m \subset \Omega$. Integrating out the remaining degrees of freedom from the configurations in Ω_m determines $p(\mathbf{r}_1, \dots, \mathbf{r}_m)$, so this function is given by Ω (or $\tilde{\Omega}$). From $c_V = k_B \langle(\Delta \ln p)^2\rangle/m$ it now follows that $c_V = c_V(\lambda)$. Since $c_V = (\partial s/\partial \ln T)_\rho$ and $s = s(\lambda)$, this implies that at fixed density $d \ln T = \phi(\lambda) d\lambda$ for some function $\phi(\lambda)$. This means that, while for two simple liquids the temperatures corresponding to the same manifold $\tilde{\Omega}$ may differ, the relative temperature changes at fixed density between different $\tilde{\Omega}$ s are the same. By integration this implies that for each simple liquid one can write $T = \Phi(\lambda)T_*(\rho)$. Combining this with the equation of state $T = f(s)h(\rho)$ shows that the function $f(s)$ is determined by λ , i.e., by the manifold $\tilde{\Omega}$. Thus

$\tilde{\Omega}(\lambda)$ quasiuniversality implies that $f(s)$ is quasiuniversal: $f(s) = f_0(s)$. The function $T_*(\rho) = h(\rho)$ is not quasiuniversal; it reflects how the liquid's characteristic energy scale depends on density [95].

Quasiuniversality of simple liquids' specific-heat temperature dependence. Eliminating λ between $c_V(\lambda)$ and $T = f_0(s(\lambda))h(\rho)$ leads to $c_V = F_0(T/h(\rho))$ for a quasiuniversal function F_0 . This is consistent with the Rosenfeld-Tarazona expression $c_V \propto T^{-2/5}$ [75], which as shown by computer simulations applies to a good approximation not only for all IPL systems, but also for LJ-type liquids and other simple liquids [96–101]. Note that $c_V \propto T^{-2/5}$ implies $s \propto -T^{-2/5}$ since $c_V = (\partial s / \partial \ln T)_\rho$ and $s \rightarrow 0$ for $T \rightarrow \infty$. This means that $f_0(s) \propto (-s)^{-5/2}$.

Quasiuniversal isochoric fragility of simple liquids. The reduced-unit relaxation time $\tilde{\tau}$ is determined by $\tilde{\Omega}$. This not only means that $\tilde{\tau}$ is a unique function of the excess entropy (“excess entropy scaling”), it also implies a quasiuniversal temperature dependence of $\tilde{\tau}$ at constant density: The quasiuniversal equation of state Eq. (7) implies that at any given density, entropy is a quasiuniversal function of temperature: $s = s(T/h(\rho))$. This implies quasiuniversality of the form $\tilde{\tau} = \tilde{\tau}(T/h(\rho))$ [95]. In particular, at constant density Angell's fragility, $-d \log_{10}(\tilde{\tau}) / d \ln T|_{T=T_g}$ [102], is a quasiuniversal number for a given cooling rate defining the glass transition temperature T_g [102–104]. This is reminiscent of the universal temperature dependence of the viscosity discussed in 1996 by Kivelson *et al.* [105], although these authors subtracted the high-temperature activation energy before demonstrating data collapsed. A quasiuniversal isochoric fragility is consistent with simulations of De Michele *et al.*, who found that different IPL systems have the same fragility [106]. The prediction is not entirely consistent with experiment, although there does seem to be a tendency that van der Waals liquids have isochoric fragilities not far from 50 [107]; in this connection it is worth noticing that it is an experimental challenge to determine the isochoric fragility accurately.

The hard-sphere system. Temperature plays no role for the configurational degrees of freedom of the HS liquid. Since only density is important, the HS phase diagram is effectively one-dimensional. This brings to mind isomorphs, the existence of which implies that a simple liquid's phase diagram is also effectively one-dimensional. Is the HS liquid simple? Since its potential energy is identically zero whereas the virial is not, the HS liquid is not simple in the sense of the term used here. In our opinion, the HS liquid should be thought of more as the $n \rightarrow \infty$ limit of an n -IPL system than as a physical liquid of its own right. When a simple liquid is modeled by a HS system, each of the liquid's isomorphs corresponds to one value of the HS packing fraction η . This establishes a one-to-one correspondence $\lambda \leftrightarrow \eta$, which explains why simple liquids' entropy, relaxation time, viscosity, etc., have been found to be quasiuniversal functions of the η parameter of the HS “reference” system.

Arguments for quasiuniversality were traditionally

based on the fact that any simple liquid is well represented by the HS reference system [7, 65, 108–112]. In the standard view, the HS system is useful because it captures the essence of liquids' harsh repulsive forces [110, 111, 113]. This picture is appealing, but runs into problems with known facts. On the one hand, IPL quasiuniversality extends down to $n = 3$ or $n = 4$, in fact for some quantities down to $n = 1$ [74, 114], where the repulsions are quite smooth. On the other hand, there are several systems with harsh repulsive forces that exhibit anomalous behavior not captured by the HS system [21–29]. From the *NVU* perspective, the HS system's usefulness is not the *explanation* of simple liquids' quasiuniversality, but a *consequence* of quasiuniversality: since all n -IPL systems are simple and quasiuniversal, the HS system inherits their simple properties because it is the $n \rightarrow \infty$ limit of an n -IPL system.

Entropy's role. Theories relating entropy to a liquid's relaxation time go back in time at least to Bestul and Chang, who in 1964 noted that the glass transitions of different glass-forming liquids occur at virtually the same value of the (excess) entropy [115]. Since the glass transition for a given cooling rate takes place when the liquid's relaxation time reaches a certain value, by generalization to other cooling rates this result implies that the relaxation time is a (quasi)universal function of entropy. Independently, based on computer simulations and analytical arguments, Rosenfeld in 1977 proposed excess entropy scaling [74]. These two results, as well as the Adam-Gibbs model from 1965 in which entropy is also crucial [116–118], may appear counterintuitive since entropy is global property: How can a global property control the relaxation time, which is determined as an average of local properties? For simple liquids $\tilde{\Omega}(\lambda)$ quasiuniversality provides a straightforward answer. Entropy *identifies* the relevant manifold $\tilde{\Omega}$, which determines the relaxation time. Accordingly, other unique markers of $\tilde{\Omega}$ should be equally useful for “determining” the relaxation time, for instance the two-particle entropy that Dzugutov in 1996 suggested controls the relaxation time [82, 119].

Characterizing $\tilde{\Omega}$ via the mean curvature. It is difficult to visualize a high-dimensional differentiable manifold. A primitive analog is a two-dimensional closed surface in ordinary three-dimensional space. Such a surface has two obvious characteristics, its area and its mean curvature. The latter is conveniently quantified in terms of the so-called (average) radius of curvature \mathfrak{R} , defined as the inverse of the curvature. Both the area and the curvature concepts generalize to multidimensional Riemannian surfaces [120–122]; fortunately pedagogical introductions to this fascinating branch of mathematics are now available [123–125]. The entropy is the logarithm of the manifold's area, but what is the physical interpretation of the radius of curvature? To answer this we start from the configuration-space canonical ensemble expression [126–128],

$$k_B T = \frac{\langle (\nabla U)^2 \rangle}{\langle \nabla^2 U \rangle}, \quad (8)$$

which is derived by partial integration of $\langle \nabla^2 U \rangle \propto \int d\mathbf{R} \nabla \cdot \nabla U(\mathbf{R}) \exp[-U(\mathbf{R})/k_B T]$. Because of ensemble equivalence, the configuration-space microcanonical ensemble may be used to calculate the averages in Eq. (8) as integrals over Ω . The inverse radius of curvature at a point on a d -dimensional hypersurface Ω is $\nabla \cdot \mathbf{n}/d$ [124, 125] where \mathbf{n} is the normal vector to Ω at the point, $\mathbf{n} = \nabla U/|\nabla U|$. To leading order in $1/\sqrt{N}$ variations in the denominator are insignificant, so this implies for the average inverse radius of curvature $1/\mathfrak{R}$ (replacing $3N-1$ by $3N$)

$$\frac{1}{\mathfrak{R}} = \frac{1}{3N} \frac{\langle \nabla^2 U \rangle}{\langle |\nabla U| \rangle}. \quad (9)$$

If the average length of the $3N$ -dimensional force vector $\mathbf{F} = -\nabla U$ is denoted by F , because fluctuations are insignificant as $N \rightarrow \infty$, one has $F^2 = \langle (\nabla U)^2 \rangle$ and Eqs. (8) and (9) imply

$$\mathfrak{R} F = 3N k_B T. \quad (10)$$

A small radius of curvature of Ω thus corresponds physically to a large average force. As $N \rightarrow \infty$, $\langle \nabla^2 U \rangle \sim N$ and $\langle |\nabla U| \rangle \sim \sqrt{N}$ which implies $\mathfrak{R} \sim \sqrt{N}$. Likewise, $F \sim \sqrt{N}$ as $N \rightarrow \infty$. If one defines $\tilde{\mathfrak{R}} \equiv \rho^{1/3} \mathfrak{R}/\sqrt{3N}$ and $\tilde{F} \equiv \rho^{-1/3} F/(k_B T \sqrt{3N})$, these two dimensionless quantities are independent of N in the thermodynamic limit and related by

$$\tilde{\mathfrak{R}} \tilde{F} = 1. \quad (11)$$

Thus the manifold $\tilde{\Omega}$'s curvature is basically \tilde{F} , a quantity that provides an alternative to the entropy for characterizing $\tilde{\Omega}$.

The entropy and \tilde{F} both have simple geometric interpretations, but the curvature \tilde{F} has the advantage of being the average of a locally defined quantity. A further advantage is that, since fluctuations are unimportant in the thermodynamic limit, \tilde{F} may be calculated from a short-time simulation. Moreover, \tilde{F} may be calculated from standard NVE or NVT simulations. We conclude that the quasiuniversal entropy dependencies observed for simple liquids' structure and dynamics may equally well be interpreted as quasiuniversal dependencies on \tilde{F} , the curvature of $\tilde{\Omega}$. Interestingly, this is the quantity that controls the relaxation time in the entropic barrier hopping theory of Schweizer and co-workers [129–131] (except for the fact that the real forces are replaced by effective forces defined by the direct correlation function).

The connection between curvature and force is intuitively obvious since motion on a flat manifold requires

no force. Indeed, the connection was made by one of the pioneers in connecting mechanics and differential geometry, Lipschitz, who wrote in 1873 [132]: “When a material particle, which is not influenced by any accelerating force, is bound to move on a given surface, the pressure exerted in each point of the trajectory is inversely proportional to the radius of curvature of this trajectory” (quoted from Ref. 133). What happens is the following. When a particle (i.e., the system) moves on a perfectly smooth surface, since no work is performed on the particle, the kinetic energy is conserved and thus the particle's velocity v is constant. This implies that the centripetal force keeping the particle on the surface, $\propto v^2/r$, is inversely proportional to the local curvature radius r .

For highly viscous liquids most motion is vibrational and one can estimate \tilde{F} by adopting a harmonic approximation. Writing for the force on a particle $-Cx$ where x is the vibrational displacement in an axis direction, one has $\langle F^2 \rangle \propto C^2 \langle x^2 \rangle$. Since $C \langle x^2 \rangle / 2 = k_B T / 2$ by equipartition, this means that if $a \equiv \rho^{-1/3}$ is the interatomic spacing, $\langle \tilde{F}^2 \rangle \equiv \rho^{-2/3} \langle F^2 \rangle / [3N (k_B T)^2] \propto a^2 / \langle x^2 \rangle = 1 / \langle \tilde{x}^2 \rangle$. Thus the quantity $a^2 / \langle x^2 \rangle$ identifies $\tilde{\Omega}$ and, in this sense, controls the relaxation time for simple liquids just as entropy does. This is an old idea [134–141], which is closely related to the reasoning behind the shoving model and other elastic models for the temperature dependence of viscous liquids' relaxation time [104, 142–144]. Note also that, since $a^2 / \langle x^2 \rangle = 1 / \langle \tilde{x}^2 \rangle$ identifies $\tilde{\Omega}$, for simple liquids the crossover to activated transitions takes place at a quasiuniversal value of the reduced-unit vibrational displacement $\langle \tilde{x}^2 \rangle$ as recently predicted by Lubchenko and coworkers [145, 146].

A single microconfiguration is enough to identify $\tilde{\Omega}$.

$\tilde{\Omega}(\lambda)$ quasiuniversality implies that the pair potential plays no role for several properties of a simple liquid, namely the isomorph invariants. This is because given an equilibrium configuration of a simple liquid $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N)$, the corresponding reduced-coordinate vector $\tilde{\mathbf{R}}$ identifies the relevant manifold $\tilde{\Omega}$. From this the isomorph invariants like entropy, specific heat, reduced diffusion constant, reduced incoherent scattering function, etc, can be calculated. The reduced-unit radial distribution function $g(\tilde{r})$ is also included in the list, of course, but this quantity is trivially given by \mathbf{R} . This illustrates again the Young-Andersen approximate scaling principle that for simple liquids knowing $g(\tilde{r})$ determines many other quantities.

IV. TOWARDS A THEORY OF SIMPLE LIQUIDS

Rosenfeld in 1977 justified IPL quasiuniversality by arguing that each n-IPL system is well represented by some HS reference system [74]. Since the HS system has just one parameter, this certainly implies IPL quasiuniversality. However, given the fact that the HS system is the $n \rightarrow \infty$ limit of n-IPL systems, this reasoning may be

regarded as circular by assuming what is to be arrived at. Section II gave one argument for quasiuniversality, but we wish here to supplement it by another argument suggesting an underlying reason for IPL quasiuniversality.

We take as starting point that the pair potential defined by a simple exponentially decaying function of r is strongly correlating, i.e., defines a simple liquid. This remains to be thoroughly investigated and documented, but the recent simulations by Veldhorst *et al.* [147] of the Buckingham potential, which has a harsh exponentially repulsive term, certainly indicates that this is the case. Thus we assume that systems with pair potentials of the form $v(r) = \varepsilon \exp(-r/\sigma)$ are strongly correlating (at least in a large part of the $(\sigma^3\rho, \varepsilon/k_B T)$ parameter space). This means that the reduced-coordinate constant-potential-energy hypersurfaces $\tilde{\Omega}$, which are *a priori* parameterized by the two dimensionless numbers $\sigma^3\rho$ and $\varepsilon/k_B T$, constitute a single-parameter family $\tilde{\Omega}(\lambda)$, where $\lambda = \lambda(\sigma^3\rho, \varepsilon/k_B T)$.

We proceed to argue that this is the quasiuniversal one-parameter family characterizing all simple liquids. It is enough to show that all IPL pair potentials have in common these reduced-coordinate constant-potential-energy hypersurfaces. Now, following the reasoning of Sec. III, there is additivity among exponentially decaying pair potentials in the sense that any linear combination of two such potentials, $C_1 \exp(-r/\sigma_1) + C_2 \exp(-r/\sigma_2)$, has the same family of reduced-coordinate constant-potential-energy hypersurfaces as a single exponential. By generalization, this implies via the mathematical identity

$$r^{-n} = \frac{1}{(n-1)!} \int_0^\infty x^{n-1} e^{-xr} dx \quad (12)$$

that the family $\tilde{\Omega}(\lambda)$ is common to the IPL potentials

and, by implication, to all simple liquids.

V. SUMMARY

The quasiuniversalities observed for simple liquids' structure, dynamics, and thermodynamics find a natural explanation in terms of quasiuniversality of the single-parameter family $\tilde{\Omega}(\lambda)$ of reduced-coordinate constant-potential-energy hypersurfaces. $\tilde{\Omega}(\lambda)$ quasiuniversality was derived for IPL systems in Sec. II, but can arrived at assuming that the exponentially repulsive pair potential is simple (Sec. IV). From IPL quasiuniversality $\tilde{\Omega}(\lambda)$ quasiuniversality generalizes to all simple liquids by virtue of their property of having strong correlations between NVT equilibrium virial and potential-energy fluctuations.

It is important to emphasize that there is no exact universality among simple liquids, only *approximate* universality. A clear demonstration of this is provided by the well-known fact that the crystalline state is only FCC for IPL exponents larger than seven (below it is BCC). Another point to be emphasized is that, in contrast to mode-coupling theory and other fully renormalized theories of liquid dynamics, the present approach does not distinguish between short and long time scales – quasiuniversality applies on all time scales (in reduced units).

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